J. Phys. Chem. Solids Pergamon Press 1962. Vol. 23, pp. 1557–1562. Printed in Great Britain.

ELECTRICAL AND OPTICAL PROPERTIES OF NATURAL STANNIC OXIDE CRYSTALS*

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(*Received* 28 *March* 1962; *revised* 7 *May* 1962)

Abstract—A survey has been made of the electrical conductivity and optical transmission properties of a number of stannic oxide crystals cut from Bolivian cassiterite. A fundamental optical energy gap, $E_G \geqslant 3{\cdot}54$ eV with a thermal shift of -6×10^{-4} eV/°K has been determined from the short wavelength cutoff. A sharp absorption at $3{\cdot}07\ \mu$ has been attributed to the presence of O–H groups oriented in a plane perpendicular to the *c*-axis of the crystal. A simple single-level, wide bandgap analysis was applied to the conductivity and Hall data in the temperature range 100° to 500°K yielding a major donor activation energy of approximately 0·7 eV for samples containing 10^{14}–10^{15} carriers/cm^3 at room temperature. Hall mobilities vary from 10 to 300 cm^2/V sec with effective masses and donor densities estimated near $0{\cdot}8\ m$ and 10^{20} cm^{-3}, respectively. Note is made of comparable parameter values observed by other investigators in film and powder specimens. No *p*-type conduction has been observed. It is concluded that stannic oxide is a broad-band semiconductor unlike the structurally similar material, rutile, which exhibits narrow 3*d*-band conduction.

INTRODUCTION

STANNIC oxide, SnO_2, is one of more than twenty assorted oxides and fluorides listed by WYCKOFF(1) as crystallizing in the tetragonal rutile structure. As such it belongs to the structural space group *P*4/*mnm* and contains two molecules per unit cell. Studies of the semiconductor properties of materials in this structural group have been largely restricted to the prototype compound, TiO_2,(2,3) for which it has been reasonably well established that extrinsic conduction based on reduction or the introduction of pentavalent and hexavalent impurities occurs by means of high effective mass electrons in a narrow 3*d*-band.(4) Intrinsic conduction has been observed above 800°K with an indicated energy gap of 3·05 ± 0·1 eV.

An interesting possibility for a different conduction mechanism is presented by stannic oxide with the $5s^25p^2$ atomic configuration possessed by the metallic constituent. It seems reasonable to expect that this material would show a more conventional broad-band conduction pattern comparable to that exhibited by zinc oxide(5) rather than one based on an unfilled inner shell structure(6) and hence it should provide a fruitful comparison material for studying the relative importance of crystal structure and metallic constituent to the determination of electrical properties.

Previous work on stannic oxide has been essentially limited to thin films(7, 8, 9, 10) and pressed or sintered powder samples.(11, 12, 13) The measurements discussed here were performed on crystalline samples of the mineral, cassiterite, in an effort to reduce the extraneous difficulties which arise from the presence of grain boundaries, inhomogeneities, and large surface-to-bulk ratios found in previous study specimens. It is the purpose of this report to provide a general survey of the results to date and to help identify important areas of investigation for further concentrated study now that synthetic crystals have become available.(14, 15)

SAMPLES

The samples used in this investigation were cut from natural crystals of Bolivian cassiterite which normally contain impure, discolored sections and smaller clear portions. Efforts at orientation were sacrificed in order to obtain workable-sized clear

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* Supported by the Office of Naval Research under Contract No. Nonr–2595(01).

specimens of maximum homogeneity which were several mm in length and width and fractions of a mm thick. However, polarizing microscope studies showed that the *c*-axis usually lay near the plane of the broad crystal face although not necessarily along the direction of conductivity measurement.

Different amounts of natural color were observed in the samples used, three general groups being evident: (a) colorless, transparent specimens, some of which took on a milky appearance due to surface or internal flaws, (b) transparent specimens showing a yellowish-orange tinge in varying degree, and (c) clear, transparent specimens exhibiting a grayish tinge when compared to those listed under group (a). Room temperature conductivities were predictable on the basis of these colors with this parameter increasing in value from group (a) to group (c). In order of magnitude, the values observed varied from 10^{-6} to 10^{1} Ω^{-1} cm^{-1}. All samples were *n*-type throughout the temperature range investigated and guard ring measurements of the surface-to-bulk conductivity ratio indicated a bulk conductivity analysis was appropriate. A spectroscopic analysis of impure scrap sample material* showed silicon, aluminum, and iron to be the most important impurities present with estimated maximums of ½ per cent.

OPTICAL TRANSMISSION

An example of the lack of homogeneity within large natural crystals is shown in Fig. 1. Sample SIA was cut off the top of a crystal furnished by the Smithsonian Institution† and Sample SII from directly beneath with no change in orientation being evident. With reference to the color groupings described in the previous section, SIA falls into group (c) and SII into group (a).

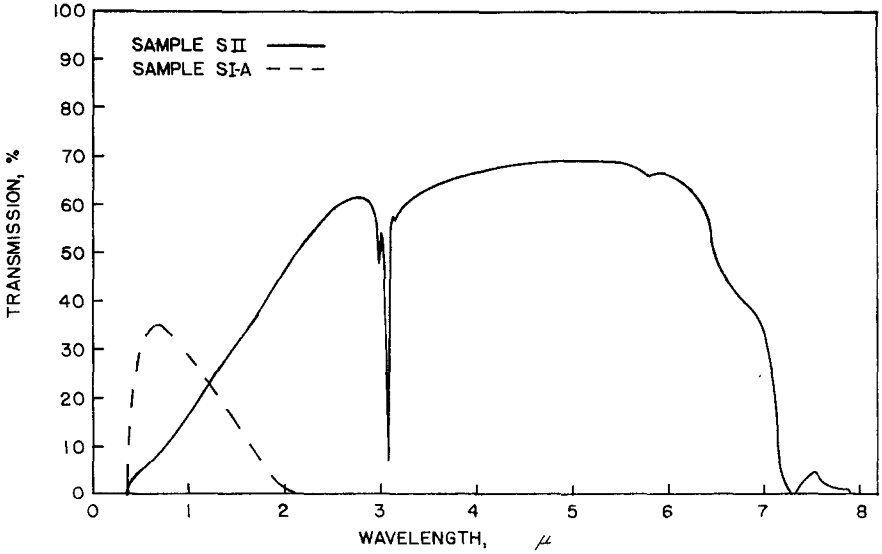

FIG. 1. Optical transmission of two cassiterite specimens.

While the only other crystalline sample studied which showed transmission characteristics similar to that of SIA was an accidental artificial crystal from the lining of a tin smelter,‡ MILOSLAVSKII(16) has reported rapid increases of absorption near 2 μ in thin film samples formed by pyrolytic decomposition of tin chloride vapors. Conductivities of these films were of the same or higher orders of magnitude than those observed in SIA and were presumed due to excess tin and/or replacement of oxygen by chloride ions.

The transmission characteristics of SII are rather typical of those observed in the host of

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[*] Analysis by The Bruce Williams Laboratories, Joplin, Missouri.

[†] Smithsonian Institution catalogue number R-8034.

[‡] Furnished by R. Weil, Laboratoire De Minerálogie et Pétrographie, Université De Strasbourg.

specimens which can be classified as belonging to color groups (a) and (b). The three most evident features of this representative optical transmission pattern are the short wavelength cutoff near 0·350 μ the sharp absorption at 3·07 μ and the long wavelength cutoff beyond 7 μ. These will be discussed in order.

1. *Short wavelength cutoff*

For samples having thicknesses of the order of $\frac{1}{2}$ mm, the shortest wavelength at which transmission was detectable was measured to be 0·350 μ. Based on the rapid increase of absorption constant in this region, a lower limit for the optical forbidden energy gap, E_G, of 3·54 eV is implied, in relatively good agreement with the value of 3·44 eV obtained from the maximum of the photoconductivity spectral response curve.(17)

The shift of the cutoff with temperature was measured for several typical specimens in the temperature range from 80°K to 415°K and an average value for $\mathrm{d}E_G/\mathrm{d}T$ of -6×10^{-4} eV/°K obtained. Linear extrapolation to 0°K leads to an absolute zero optical energy gap of approximately 3·7 eV.

For purposes of comparison, the values of E_G and $\mathrm{d}E_G/\mathrm{d}T$ obtained by CRONEMEYER(2) for titanium dioxide are 3·05 eV and $-9{\cdot}5\times10^{-4}$ eV/°K and by MOLLWO *et al.*(18) for zinc oxide, 3·2 eV and $-9{\cdot}5\times10^{-4}$ eV/°K.

2. *Absorption at* 3·07 μ

All samples which transmitted light beyond 2·5 μ showed a sharp absorption at 3·07 μ. An additional absorption dip usually appeared on the short wavelength shoulder at 2·98 μ although it had a variable intensity from sample to sample, being almost imperceptible for specimens at the low end of the conductivity range studied and greatly enhanced for those of higher conductivity.

Transmission in this wavelength region was also observed under polarized light. The main and satellite absorptions disappeared when the observed light was polarized parallel to the crystalline optic axis. Similar optical absorptions have been observed both in rutile(19) and in quartz(20) and have been rather definitely attributed to absorption by O–H stretching vibrations. The above results imply that O–H groups are also present in natural stannic oxide—presumably having been introduced during a natural hydrothermal growth process—and that they are oriented in a plane perpendicular to the *c*-axis of the crystal.

3. *Long wavelength cut-off region*

Normal specimens belonging to color groups (a) and (b) showed an apparent cutoff at wavelengths ranging from 7·2 to 7·3 μ. As is evident from Fig. 1, this is the edge of a sharp absorption with a slight transmission having a maximum at 7·55 μ reappearing beyond this point in the thinner samples. The maximum cutoff observed to date is 8·62 μ in the thinnest sample used. Since the absorptions have been observed on a variety of crystals and show a dependence upon the polarization of the observed light, it appears likely that they are subsidiary bands of the main lattice absorption. This is further reinforced by the observation(2) that the cutoff for rutile is in the same wavelength region.

ELECTRICAL CONDUCTIVITY AND HALL EFFECT

Figure 2 gives the results of conductivity

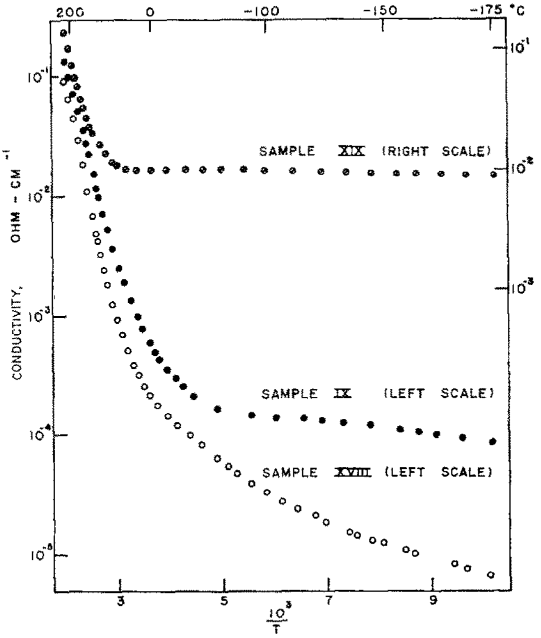

FIG. 2. Typical conductivity vs. reciprocal temperature data.

measurements on three cassiterite specimens in the temperature range from 100°K to 500°K. As mentioned previously, Sample XIX belongs to color group (b). On the other hand, Samples IX and XVIII can be classified in group (a).

Based on a relation of the form $\sigma = \sigma_0 \exp(-\epsilon/2kT)$, the conductivity activation energy, ϵ, shows a value of 0·72 eV in the straight line portion at higher temperatures for all three samples. This compares favorably with the value of 0·77 eV calculated from the data of Foex(13) for pressed samples of stannic oxide powder prepared by the oxidation of tin with nitric acid, followed by a heat treatment in air at 1200°C. Foex's room temperature conductivities were three to four orders of magnitude below those reported here. For thin film samples with conductivities four to five orders of magnitude above those reported here, Miloslavskii(16) calculates an activation energy of 0·12 eV in the same temperature range. Degeneracy and impurity band formation are described as factors in the latter case.

To provide information concerning charge carrier densities and mobilities, Hall effect measurements were carried out simultaneously with the conductivity runs. A simple, two-probe Hall circuit was used. Problems in maintaining good contact to the Hall probes with an indium–gallium amalgam effectively limited the range of usable Hall data to 0°C and above. Although samples were maintained at elevated temperatures for tens of hr during the measurements, datum points taken upon increase and decrease of temperature showed excellent reproducibility.

The trend of Hall mobility ($R\sigma$) values with temperature is given in Fig. 3. It should be noted that the high temperature mobility variation is not greatly different from the $T^{-1\cdot5}$ dependence to be expected from a simple lattice scattering mechanism. For Sample XIX, the increase in mobility with decreasing temperature extended well beyond the leveling-off point in the conductivity curve. The rapid decrease for Sample IX below 100°C may be associated with the presence of visible interior flaws.

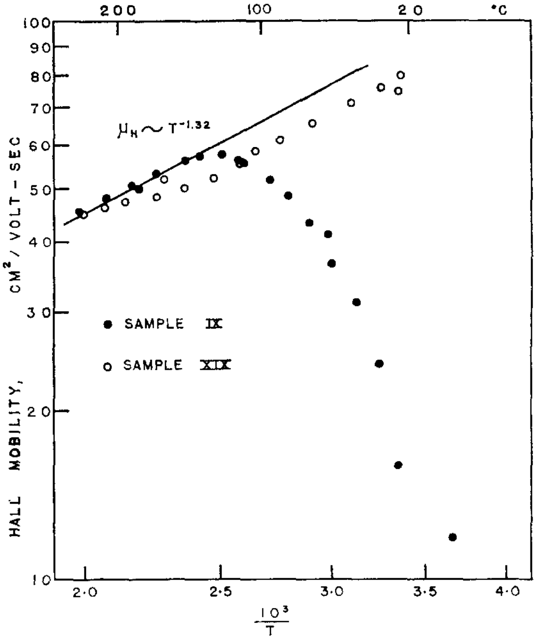

Fig. 3. Hall mobility vs. reciprocal temperature.

In an attempt to provide insight into the energy level characteristics of these specimens, a classical, wide bandgap, single-level semiconductor analysis was applied to the Hall data. On this basis the high temperature slope of the log $RT^{3/4}$ plot vs. $1/T$ should give the donor activation energy/2, assuming that the Fermi level is several kT above the impurity levels with only a small fraction of the donors ionized and that if another donor level is present much nearer the conduction band, the number of conduction electrons it furnishes is small compared to those being excited from the lower level. A further assumption of small variation of the Fermi level energy with temperature in the region of interest allowed estimates to be made of the donor density and the density-of-states effective mass for which no independent measure was available.

While it is not suggested that this calculation permits a high degree of accuracy in the determination of m_e and N_d, it is felt to be justified for establishing orders of magnitude. Values of the parameters of interest are given in Table I. The conductivities, Hall mobilities and carrier densities listed are for room temperature. It may be noted that Miloslavskii and Lyashenko(21) have also reported fractional effective masses calculated from the optical constants of their thin film samples. Their values are lower by a factor of approximately three.

The foregoing analysis was based upon the presence of donors alone. An alternative approach is necessary if the donors are largely compensated by acceptors. Here the slope of the log $RT^{3/2}$ vs. $1/T$ curve would be used to obtain magnitudes for ϵ_d. The appropriate values are 0·31 and 0·33 eV for Samples IX and XIX, respectively.

Table 1. *Conduction parameters*

Sample	IX	XVIII	XIX	SIA
Conductivity:				
σ (Ω^{-1} cm^{-1})	1×10^{-3}	3×10^{-4}	1×10^{-2}	60
Carrier Density:				
n_e (cm^{-3})	4×10^{14}	$3{\cdot}5 \times 10^{14}$	8×10^{14}	$1{\cdot}2 \times 10^{18}$
Hall Mobility:				
$R\sigma$ (cm^2/V sec)	15	7	80	315
Donor Densities:				
N_d (cm^{-3})	$1{\cdot}1 \times 10^{20}$	not available	$1{\cdot}4 \times 10^{20}$	not available
Effective Mass:				
m_e (electron masses)	0·65	not available	0·91	not available

At the present time, neither the existing data nor a suitable theory concerning the origin of the donor states allows a definitive choice to be made between the two possibilities. However, the latter seems less likely since a very high degree of compensation would indicate the possibility of observing p-type conduction in random specimens and this has not occurred.

A further point is important. The density-of-states effective mass calculated using the compensated semiconductor analysis will have a *maximum* value equal to that given in Table I.

DISCUSSION AND CONCLUSIONS

Considering the nature of the specimens studied, it must be emphasized that the results given above can provide only a very preliminary step in the description of the conduction mechanism exhibited by stannic oxide. However, in view of the reproducibility of results on individual samples and between samples obtained from different sources at different times, as well as the comparable magnitude of certain of the parameters reported by other investigators on film and powder samples, it is expected that there will be a significant carryover of interpretation to observations on syntheric material. This will be particularly true, of course, for oxygen-deficient and highly doped specimens.

Some degree of success has been achieved in correlating optical and electrical data. Clearly the conductivity observed near 500°K is extrinsic in character. The data of FOEX(13) above 1000°K provide intrinsic activation energies ranging from 3·74 to 4·0 eV depending upon whether the sample was heated in an atmosphere of oxygen or in a vacuum. The first value is in good agreement with the 0°K extrapolation of the forbidden energy gap.

The assignment of the value 0·7 eV to the donor activation energy in the preceding section is favored by optical transmission results at wavelengths less than 2 μ. Sample SII of Fig. 1 gives a typical example of the transmission decrease approaching the short wavelength cutoff. In the lowest conductivity specimen studied, a distinct transmission plateau centered at 1·6 μ (0·77 eV) was observed. The nature of the donor centers is unknown. At present they would appear to be due to a complex combination of oxygen vacancies, interstitial impurities and O–H groups. Extension of conductivity measurements to higher and lower temperatures and to selectivity doped synthetic samples is needed to clarify the situation.

While the 3·07 μ absorption is attributed to the presence of O–H groups, the magnitude of secondary absorptions increases with increasing impurity content and room temperature conductivity. The suggestion is made that the usual O–H stretching frequency is slightly modified when the group finds itself in close proximity to an ion foreign to the lattice. This is a situation which occurs with high probability when the density of donor states is large.

The magnitude of the optical absorption beyond 2 μ shows only a very slight increase with temperature below 500°K indicating that free electron absorption is not significant for carrier densities below 10^{16} cm^{-3}. Above a density of 10^{18} cm^{-3} as exhibited by Sample SIA, the effect is large. THOMAS(22) places a lower limit of 5×10^{17} cm^{-3} on the onset of free carrier absorption in zinc oxide and MILOSLAVSKII and LYASHENKO(21) have observed a linear dependence of the absorption coefficient on electron concentration in stannic oxide thin film samples. Their data includes no specimens with electron densities less than 10^{19} cm^{-3}.

An inspection of Fig. 2 shows that a pattern of increasing conductivity change with decreasing room temperature conductivity is followed in the lower temperature range. The concept of degeneracy is invalid in view of the low carrier densities involved. Results on Sample XIX might be explained in terms of a minor donor level very near the bottom of the conduction band which is fully ionized at the lowest temperatures attained. An interpretation of the decreasing conductivity of color group (a) Samples IX and XVIII on the same basis would require a decrease in charge mobility for which there is some evidence in Fig. 3. On the other hand, the high densities of major donors calculated suggests the possibility of impurity band formation. Paradoxically, however, the higher conductivity specimens show the higher mobilities, leaving the question open for further study.

In reference to the introductory remarks, the fractional effective mass observed here and by other investigators on a different form of the material, the magnitudes of the mobility and major donor activation energy, all lead to the conclusion that stannic oxide behaves as a relatively straightforward, broad-band semiconductor in the extrinsic conductivity region above room temperature.

Acknowledgements—The author wishes to thank J. E. HURT, A. J. BELSKI, K. M. PROCTOR and E. E. TOLLY, graduate students at Oklahoma State University, for their assistance in obtaining the experimental data reported and to express his gratitude to the Physics Branch of the Office of Naval Research for providing the financial support which made this work possible.

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